

PROCEEDINGS OF THE XX ALL-RUSSIA CONFERENCE  
ON PHYSICS OF FERROELECTRICS (VKS-XX)  
(Krasnoyarsk, Russia, August 18–22, 2014)

## Elastic, Dielectric, and Piezoelectric Properties of Ceramic Lead Zirconate Titanate/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Composites

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**Abstract**—The technology of producing ceramic lead zirconate titanate/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composites has been developed. Elements of piezoactive composites containing from 0 to 60 vol %  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been prepared. The elastic, dielectric, and piezoelectric parameters of the synthesized ceramic composites have been measured, and their microstructure has been studied. It has been found that the concentration dependences of the elastic and piezoelectric properties exhibit anomalies. The obtained data have been interpreted based on the percolation theory and the concept of microstructural constructing polycrystalline composition materials.

DOI: 10.1134/S1063783415030270

### 1. INTRODUCTION

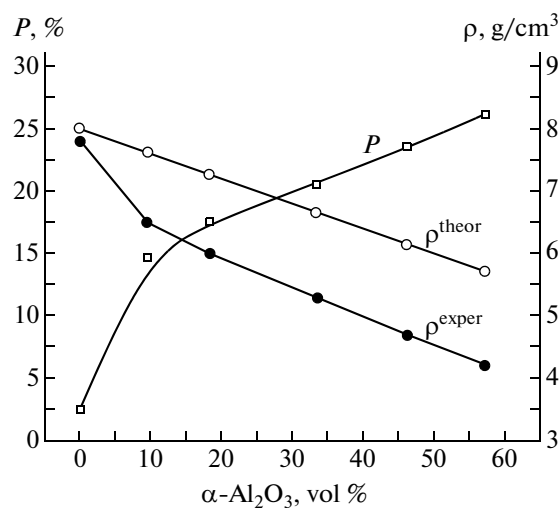
In recent years, mechanical properties of ceramic materials have been significantly improved using the technology of ceramic composites. Structural ceramic composites with improved mechanical and thermal properties are widely used in the aerospace, automobile, and power industry [1, 2]. It was also shown in [3, 4] that small additions of nanopowders of barium and neodymium titanates, lithium titanate, and also other ferroelectric materials into Al<sub>2</sub>O<sub>3</sub> and other structural ceramics' increase the impact toughness and the strength of ceramic composites by several times.

It is found [5, 6] that the presence of a second passive phase in ceramic piezocomposites substantially improves the mechanical and electrical properties of a piezoceramic matrix. However, the problem of compromise of properties, namely, the deterioration of the piezoelectric properties with increasing the passive phase concentration due to the change in the ceramics microstructure (suppression of grain growth and, as a result, clamping domains and decrease in their mobility) remain unsolved.

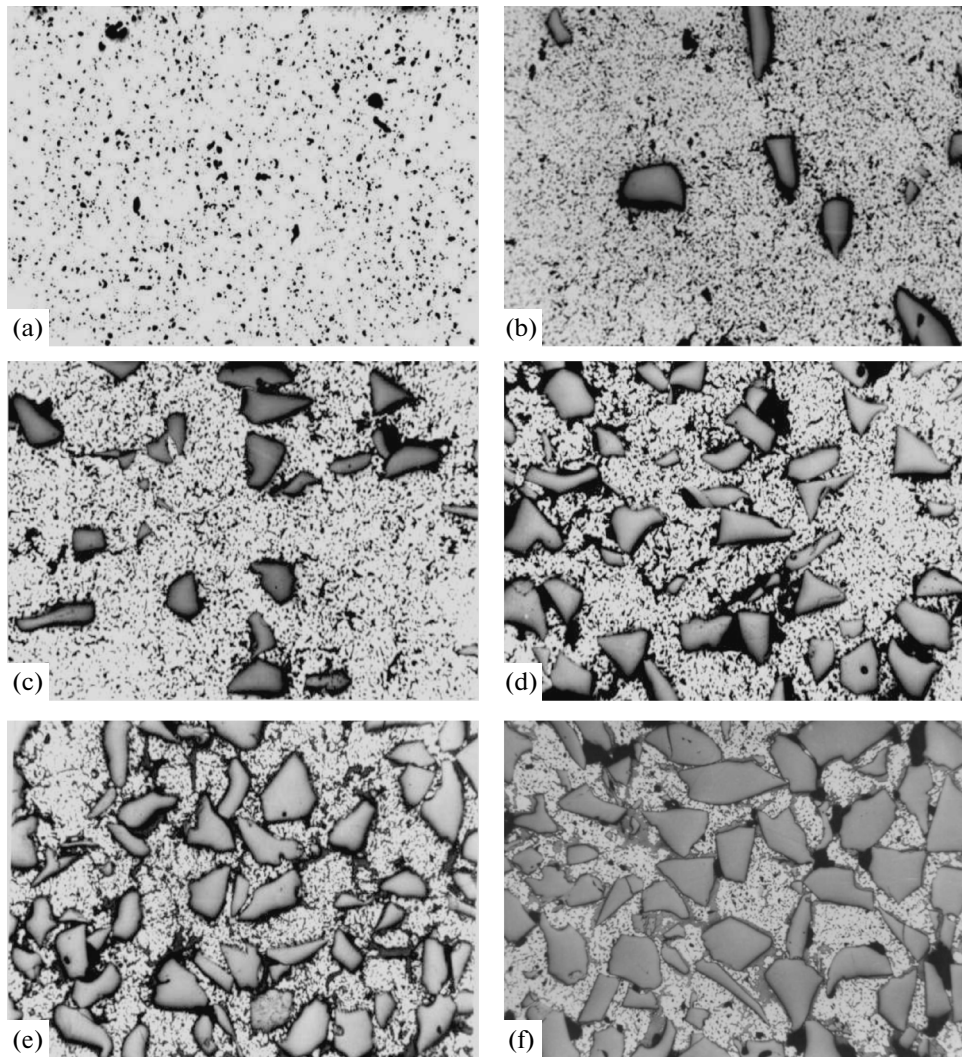
The aim of this work is to develop the technology of producing and to study the elastic, dielectric, and piezoelectric parameters, and the microstructure of ceramic composites LZT/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (LZT is for lead zirconate titanate) over wide  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> concentration range from 0 to 60 vol %.

### 2. TECHNOLOGY OF PRODUCING COMPOSITES AND MEASUREMENT METHODS

The initial components for preparing ceramic composites LZT/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were a synthesized powder PKR-1 and a crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) powder. The average size of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites was 140–150  $\mu$ m. The powders PKR-1 and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were subjected to specific heat and chemical treatments for their passivation and decrease in the reactivity. The powder were mixed using a special technique [7, 8],



**Fig. 1.** Dependences of theoretical  $\rho^{\text{theor}}$  and measured  $\rho^{\text{exper}}$  densities and relative porosity  $P$  of ceramic PKR-1/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composite on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> volume concentration.



**Fig. 2.** Optical photomicrographs of the polished surface of ceramic PKR-1/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composites at various  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> volume concentrations: (a) 0 vol %, usual sintering, magnification 65 $\times$ ; (b) 10 vol %, magnification 50 $\times$ ; (c) 18 vol %, magnification 50 $\times$ ; (d) 33 vol %, magnification 50 $\times$ ; (e) 46 vol %, magnification 50 $\times$ ; and (f) 57 vol %, magnification 50 $\times$ .

giving the homogeneous distribution of the components without additional refining and fracturing the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites. The mixture was sintered under the same conditions corresponding to the common conditions of sintering of the PKR-1 material.

The parameters of the piezoelements were measured using the standard resonance–antiresonance method and the analysis of the impedance spectra [9]. The microstructure studies were performed on polished metallographic sections of the samples using a NEOPHOT-21 microscope of reflected light.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the dependences of theoretical  $\rho^{\text{theor}}$  and measured  $\rho^{\text{exper}}$  density and also the relative poros-

ity  $P$  of the ceramic composite PKR-1/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the volume concentration of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

It is seen from Fig. 1 that the relative porosity of the ceramic sample increases quickly, as the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> concentration increases from 0 to 10 vol %, and, then, it increases almost linearly with increasing the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> contents to 60 vol %. This fact is explained by the existence of non-shrinking  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase that prevents shrinking of the ceramic matrix during sintering and leads to the occurrence of a microporosity.

The shape and the distribution of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallites and also pores on the polished metallographic sections of common ceramics PKR-1 and composite PKR-1/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with various  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> contents are shown in the photomicrographs (Fig. 2). The porosity of the PKR-1 piezoceramics produced by common sintering (Fig. 2a) is not higher than 3–4%.

The pores have predominantly an isometric shape and the average size 4  $\mu\text{m}$ . Unlike this, the porosity of piezoelectric matrix in the composite samples substantially increases even at low contents of  $\alpha\text{-Al}_2\text{O}_3$  particles (10 vol %) (Figs. 2b–2f). It is due to a sharp increase in the number of pores and due to the increase in their average size (to 10–12  $\mu\text{m}$ ). As the concentration of  $\alpha\text{-Al}_2\text{O}_3$  particles increases, the composite porosity increases gradually and the pore size increases; in addition, the elongated pores become branched. Thus, we should consider all the dependences of the elastic, dielectric, and piezoelectric parameters of the ceramic composites on the  $\alpha\text{-Al}_2\text{O}_3$  content, taking into account the experimentally observed formation and increase in the relative porosity of the composite, along with the influence of the non-piezoelectric  $\alpha\text{-Al}_2\text{O}_3$  phase exhibiting specific properties ( $\epsilon_{33} = 10.55$ ,  $\rho = 4 \text{ g cm}^{-3}$ , sound velocity  $V_l = 11.2 \text{ km s}^{-1}$ ). The collective effect can have certain peculiarities, and it is not a simple sum of the above noted effects, because of cardinal change in the microstructure and the influence of intermediate layers at the  $\alpha\text{-Al}_2\text{O}_3$  crystal/piezoelectric matrix interface.

Figure 3 shows the dependences of piezoelectric moduli  $d_{33}$  and  $d_{31}$  and relative permittivity  $\epsilon_{33}^T/\epsilon_0$  of the ceramic composite PKR-1/ $\alpha\text{-Al}_2\text{O}_3$  on the volume  $\alpha\text{-Al}_2\text{O}_3$  concentration.

The relative permittivity  $\epsilon_{33}^T/\epsilon_0$  of the porous ceramics decreases quickly with increasing the  $\alpha\text{-Al}_2\text{O}_3$  concentration, which is due to the increase in the porosity and the content of the non-piezoelectric  $\alpha\text{-Al}_2\text{O}_3$  phase (the permittivities of the piezoceramics,  $\alpha\text{-Al}_2\text{O}_3$ , and the gas medium inside the pores are different substantially). As the  $\alpha\text{-Al}_2\text{O}_3$  concentration increases, the behavior of the composite piezoelectric modulus  $d_{33}$  is determined by the competing influence of the increase in the porosity and the content of the nonpiezoelectric phase. The piezoelectric modulus  $d_{33}$  increases in the range 0–20 vol %  $\alpha\text{-Al}_2\text{O}_3$  because of fast increase in the porosity (Fig. 1). The cause of increasing  $d_{33}$  in the porous ceramics is the better polarization of the elements due to lightening of non-180° domain reorientations because of removal mechanical stresses and faster and more reliable fixation of domain walls at the pore boundaries [9, 10]. The experimental value of  $d_{33}$  of the porous PKR-1 ceramics at the relative porosity 20% is 300 pC/N (typical value for the hot-pressed PKR-1 ceramics is 250 pC/N). Further increase in the  $\alpha\text{-Al}_2\text{O}_3$  concentration leads to the decrease in  $d_{33}$  because of the increase in the content of the non-piezoelectric phase at more slowly increased porosity (the decrease in the relative area of the piezoactive phase is not compensated by the increase of the specific pressure on the

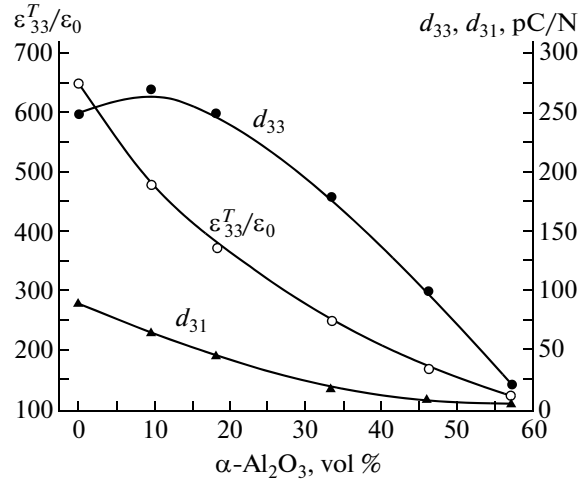
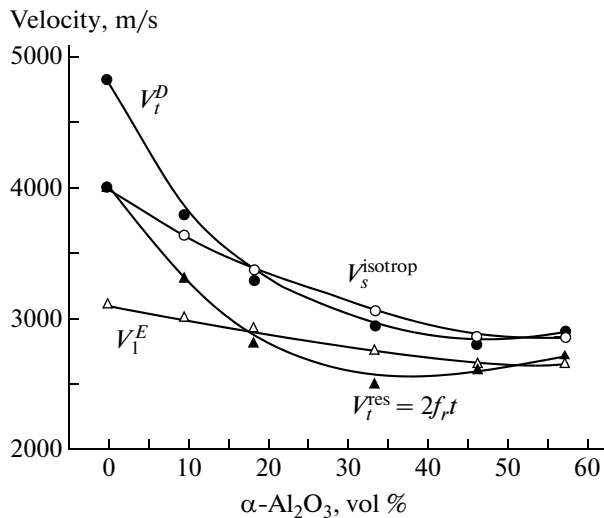


Fig. 3. Dependences of piezoelectric moduli  $d_{33}$  and  $d_{31}$  and relative permittivity  $\epsilon_{33}^T/\epsilon_0$  of the ceramic PKR-1/ $\alpha\text{-Al}_2\text{O}_3$  composite on the  $\alpha\text{-Al}_2\text{O}_3$  volume concentration.

ceramic skeleton, because the elastic rigidity of  $\alpha\text{-Al}_2\text{O}_3$ , unlike air, cannot be neglected). Piezoelectric modulus  $d_{31}$  of the composite decreases fast as a result of increasing the content of non-piezoelectric phase and the porosity increase (violation of the connectivity of the porous ceramics in the longitudinal direction).

Figure 4 shows the dependences of the propagation velocities of elastic vibrations of the thickness mode  $V_t^D$ , the longitudinal mode  $V_l^E$ , the thickness mode  $V_t^{\text{res}} = 2f_t t$ , and the longitudinal mode of the non-polarized element  $V_s^{\text{isotrop}}$  (5 MHz) for the ceramic PKR-1/ $\alpha\text{-Al}_2\text{O}_3$  composite on the volume  $\alpha\text{-Al}_2\text{O}_3$  concentration.

It is seen from Fig. 4, that all the propagation velocities of elastic vibrations (thickness mode, longitudinal mode, and the longitudinal mode of non-polarized element) decrease as the  $\alpha\text{-Al}_2\text{O}_3$  concentration increases up to 40–50 vol %. As the expected percolation threshold is approached, the decrease in the velocities is retarded, and they begin to increase slowly. Velocities  $V_l^E$  and  $V_s^{\text{isotrop}}$  decrease more slowly than velocities  $V_t^D$  and  $V_t^{\text{res}} = 2f_t t$ . A clear cause of different behaviors of the longitudinal and thickness vibration modes is the size factor. The formation of  $\alpha\text{-Al}_2\text{O}_3$  clusters and bridges in the transverse direction is less probable than that in the thickness direction of the standard samples. At least, it must set in at higher  $\alpha\text{-Al}_2\text{O}_3$  concentrations in the latter case. As follows from Fig. 4, the porosity increase in the PKR-1/ $\alpha\text{-Al}_2\text{O}_3$  composite is a prevailing factor that determines the behavior of elastic wave velocities. At the sintering temperatures used in this study,  $\alpha\text{-Al}_2\text{O}_3$  crystallite



**Fig. 4.** Dependence of the speed of propagation of elastic vibrations of thickness mode  $V_t^D$ , longitudinal mode  $V_1^E$ , thickness mode  $V_t^{\text{res}} = 2f_r t$ , and longitudinal mode of non-polarized element  $V_s^{\text{isotrop}}$  (5 MHz) for the ceramic PKR-1/ $\alpha\text{-Al}_2\text{O}_3$  composite on the  $\alpha\text{-Al}_2\text{O}_3$  volume concentration.

cannot form a dense  $\text{Al}_2\text{O}_3$  ceramics, and the ceramics is an aggregate of weakly-bounded crystallites with substantial porosity even at the  $\alpha\text{-Al}_2\text{O}_3$  concentration 100%. Despite the formation of the  $\alpha\text{-Al}_2\text{O}_3$  clusters and continuous bridges (Fig. 2f) near the percolation threshold,

The acoustic and mechanical contact between the  $\alpha\text{-Al}_2\text{O}_3$  crystallites is insufficient for the elastic wave velocities to increase sharply. In addition, the difference between the elastic moduli of  $\alpha\text{-Al}_2\text{O}_3$  and LZT is insufficient for the classical percolation effects to be observed clearly.

#### 4. CONCLUSIONS

In this study, we developed the technology of producing ceramic LZT/ $\alpha\text{-Al}_2\text{O}_3$  composites based on our concept of microstructural constructing polycrystalline composite materials proposed in [7, 8].

The results allowed us to state that the introduction of the passive non-shrinkage phase in the piezocer-

amic matrix leads to the formation of microporosity that substantially influences the ceramic composite parameters. It is shown that the obtained dependences of the elastic, dielectric, and piezoelectric parameters of the ceramic composites on the  $\alpha\text{-Al}_2\text{O}_3$  content are determined by the competing influence of the increase in the relative porosity of the ceramic matrix and the increase in the content of the non-piezoelectric  $\alpha\text{-Al}_2\text{O}_3$  phase.

It was found that the LZT/ $\alpha\text{-Al}_2\text{O}_3$  ceramic composites containing to 20% of the passive phase exhibit the improved electrophysical and mechanical properties as compared to those of the initial ceramics, which make it possible to use them as active elements of piezoelectric devices and ultrasonic sensors. The designed ceramic composites were used to manufacture piezoelectric elements with a resonance frequency to 10 MHz and broadband transducers for nondestructive control with enhanced efficiency and wear resistance.

The developed technology can be considered as one of alternative methods of producing porous ceramics and is the basis for designing new generation of polycrystalline composite materials for promising ultrasonic, piezoelectric, and “smart” applications.

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*Translated by Yu. Ryzhkov*